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One-Pot Electrosynthesis of Substituted Imidazolinium and Tetrahydropyrimidinium Salts from Secondary Alkyldiamines: An Electrochemical Route toward Ionic Liquids

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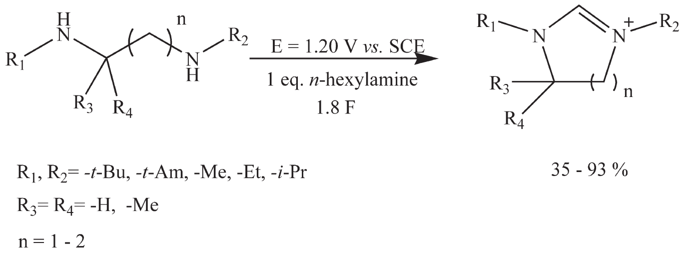

A one-pot electrosynthetic procedure has been developed to afford imidazolium and tetrahydropyrimidinium cationic derivatives from secondary alkyl diamines in neutral media. To this end, electrochemical oxidation of a series of aliphatic diamines (**1**−**9**) has been investigated. Mechanistic information is provided from analysis of the cyclic voltammetry data and identification of intermediate species and final products. The coexistence of two first-order chemical reactions, C_α−H and C_α−C_β, at the radical cation level leading to identical final products is suggested to justify not only the nature but also the yields of the salts obtained.

Introduction

Room-temperature ionic liquids [RTILs; e.g., salts of quaternary ammonium, phosphonium, or pyridinium cations with inorganic counterions (BF_4^-, PF_6^-, $CFSO_3^-$) are molten salts with melting points below 100 °C. RTILs[1] have attracted much interest in recent years because of their low pressure, chemical and thermal stability, solvating ability, nonflammability, and ability to act as catalysts. Furthermore, they have frequently been used as "green" reaction media in clean organic synthetic processes as substitutes for conventional toxic and volatile solvents. Other properties, such as high ionic conductivity and electrochemical stability have led to their use as solvents in many solution electrochemistry studies,[2] electrodeposition,[3] electro-polymerization[4] and as electrolytes in electrochemical devices, such as batteries,[5] capacitors,[6] fuel cells,[7] and solar cells.[8] Furthermore, ionic liquids have attracted the attention of researchers of lithium batteries as novel candidates for electrolyte solvents with thermal stability.[9] Several ionic liquid electrolytes based on alkylpyrimidinium,[9d] alkylpyrrolidinium,[9e] and methoxyethyl-substituted

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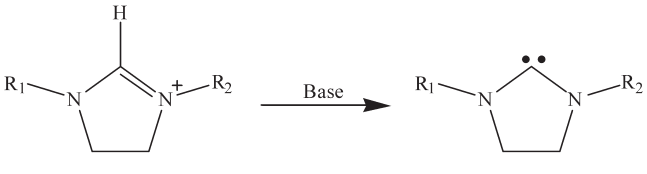
quaternary ammonium[9c] cations have been reported to be compatible with lithium battery systems. Most imidazolium-based ionic liquids are not only nonflammable but also stable in a broad temperature range from room temperature to over 400 °C, have good fluid properties as versatile solvents, and suffer from low cathodic stability since they decompose irreversibly on negative electrode surfaces.[10]

Moreover, substituted imidazolium and tetrahydropyrimidinium cations are commonly used as precursors of stable *N*-heterocyclic carbenes, which have been widely employed as ligands for transition-metal catalysts and as organic catalysts in their own right.[11] Deprotonation of these carbene precursor salts with strong bases has been proven to be a reliable route for affording a large variety of stable carbenes (Scheme 1). Recently, the chemical synthesis of an imidazolinium salt bearing a phenyl ring at the C2-position has been described,[12] which is particularly interesting in some applications since an undesired deprotonation as outlined in Scheme 1 cannot occur.

Several synthetic methods have been well-established to prepare *N*,*N*′-dialkylaminium salts.[13] However, the separation of the salts obtained by using these methods is extremely complicated especially due to the difficulty of isolating them from ammonium salt byproduct. Previous electrochemical investigations have shown the possibility of obtaining imidazolium-based ionic liquids from the appropriate diamine.[14] Such studies have demonstrated that consumption of electrocatalytic amounts of charge (0.1 F) given the reaction time required affords the secondary alkyl diamines reported in very good yields (90%) as depicted below (step 1, Scheme 2). On the other hand, a significant decrease in the yield of the aforementioned diamines obtained (67%) was observed, and new imidazolinium ions (18%) were identified when exhaustive electrolysis (0.7 F) were performed in similar experimental conditions (step 2, Scheme 2). It would be reasonable to suggest that imidazolium ions were products of the electrochemical oxidation of these diamines.

SCHEME 1



R_1, R_2 = -H, -alkyl

This publication[14] was mostly focused on the electrochemical behavior of di-*tert*-alkylamines leading to a new way of affording highly hindered secondary alkyl diamines. Such preliminary results were simultaneously the starting point for the present work, eventually resulting in the development of a novel electrosynthetic route toward imidazolium and tetrahydropyrimidinium cation salts from secondary alkyl diamines. This paper deals with the study of the anodic oxidation of a series of secondary alkyl diamines (**1**−**9**), shown in Figure 1. The experimental conditions employed have been optimized in order to obtain the maximum yields of the desired compounds. To this aim, the influence of the media will be carefully discussed.

Results and Discussion

We focus our discussion of the electrochemical behavior and mechanistic proposal on the experimental data obtained for **1**. Knowing the basic character of functional aliphatic amino groups,[14,15] the effect of the presence of protons on the electrochemical oxidation behavior of a series of aliphatic diamines is discussed below.

Cyclic Voltammetry in Neutral Media. A characteristic cyclic voltammogram of **1** (4.00 mM) at slow scan rates in DMF + $LiClO_4$ 0.1 M shows two consecutive chemically irreversible anodic peaks located at 1.13 and 1.53 V vs SCE, respectively (Figure 2a). The oxidation peak potential of the first anodic wave shifted toward more positive potentials as the scan rate (v) increased. A plot of E_{Pa1} versus log v showed a linear dependence ($\partial E_{Pa1}/\partial \log v = 48$ mV). On the other hand, the current function ($I_{Pa1}/cv^{1/2}$) for that peak decreased with $v^{1/2}$, which confirms the presence of a coupling chemical reaction following the electron-transfer process. The anodic current at slow scan rates corresponds to the transfer of 1.3 electrons per molecule. The reversibility of the first anodic peak was reached by increasing the scan rate to 70 V s^{-1}, and the oxidation process became monoelectronic

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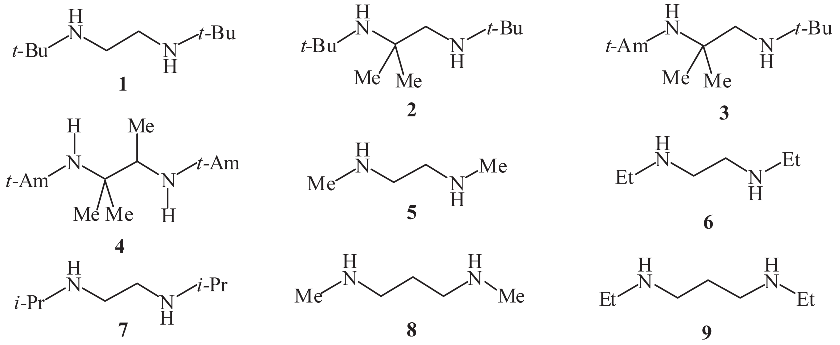
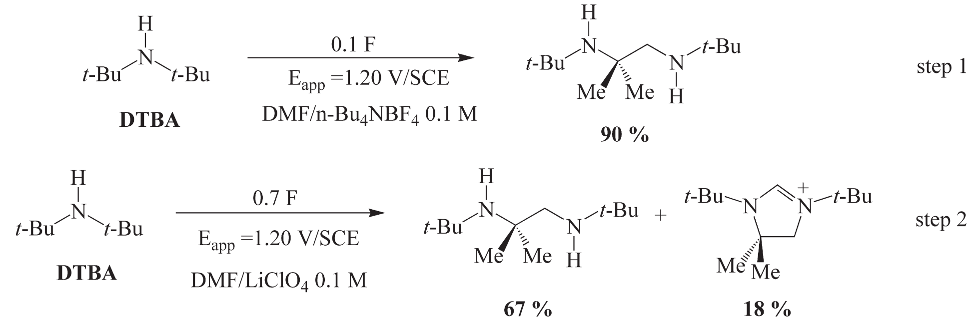


FIGURE 1. Alkyl diamines **1**−**9** employed in the electrochemical study.

SCHEME 2



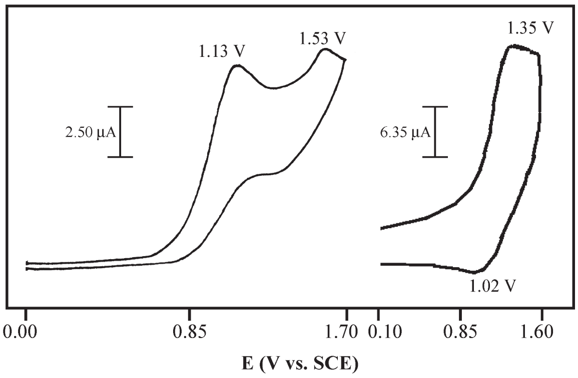


FIGURE 2. Cyclic voltammogram of **1** (4.00 mM) in DMF + $LiClO_4$ 0.1 M on a glassy carbon electrode (d = 0.5 mm): (a) 0.1 V s^{-1}, (b) 70 V s^{-1}.

(E_1^0 = 1.16 V). Furthermore, the second anodic peak disappeared when the reversibility of the first voltammetric signal was observed (Figure 2b). Such experimental evidences suggested the presence of a chemical reaction following the first electron transfer and an ECE mechanism at the level of the first anodic wave.[16] According to the standard potential value, E_1^0 = 1.16 V, the first wave should be ascribed to the oxidation of a secondary alkyl amino group.[14] At this point, it is possible to suggest the deprotonation of the radical cation, $\mathbf{1}^{\bullet+}$, as the chemical reaction of C_α−H bond cleavage coupled to the electron transfer. The oxidation peak at 1.53 V can be attributed to the oxidation of the corresponding monoprotonated species, $\mathbf{1H}^+$, formed as a result of the chemical reaction between **1** and the $\mathbf{H}^+$ formed from the C_α−H bond cleavage at the radical cation level.

Cyclic Voltammetry in Basic Media. *N*-Hexylamine, which undergoes an irreversible monoelectronic process at 1.45 V on the anodic scan, is employed as a base in this media.[14] The disappearance of the second oxidation peak observed for **1** (4.00 mM) in DMF + $LiClO_4$ 0.1 M when cyclic voltammetric experiments were performed in the presence of *n*-hexylamine should be expected since the formation of $\mathbf{1H}^+$ should be minimized under such experimental conditions.

The analysis of the voltammetric data was somewhat complicated when *n*-hexylamine was added to a solution containing **1**. However, some useful conclusions could be obtained from these experiments when the amount of *n*-hexylamine present in solution was limited to 1 equiv or less. Thus, upon addition of 0.5 equiv of *n*-hexylamine a progressive decrease was observed in the height of the second anodic peak obtained for **1** suggesting that $\mathbf{1H}^+$ was no longer formed in solution when enough *n*-hexylamine was added. Accordingly, the addition of up to 0.5−1.0 equiv of *n*-hexylamine resulted in a progressive decrease in that voltammetric signal and subsequent increase in the first oxidation peak located at 1.13 V, the height of which corresponds to the transfer of 1.8 electrons, slightly less intense than expected for a bielectronic process. Reversibility of the oxidation peak was observed by increasing the scan rate to 100 V s^{-1} leading to a monoelectronic process (E_1^0 = 1.16 V). Strong distortion was observed in the shape of the cyclic voltammograms when adding amounts of *n*-hexylamine larger than an equivalent to a solution initially containing **1**. A second broad peak clearly emerged probably due to the presence of neutral *n*-hexylamine which is oxidized

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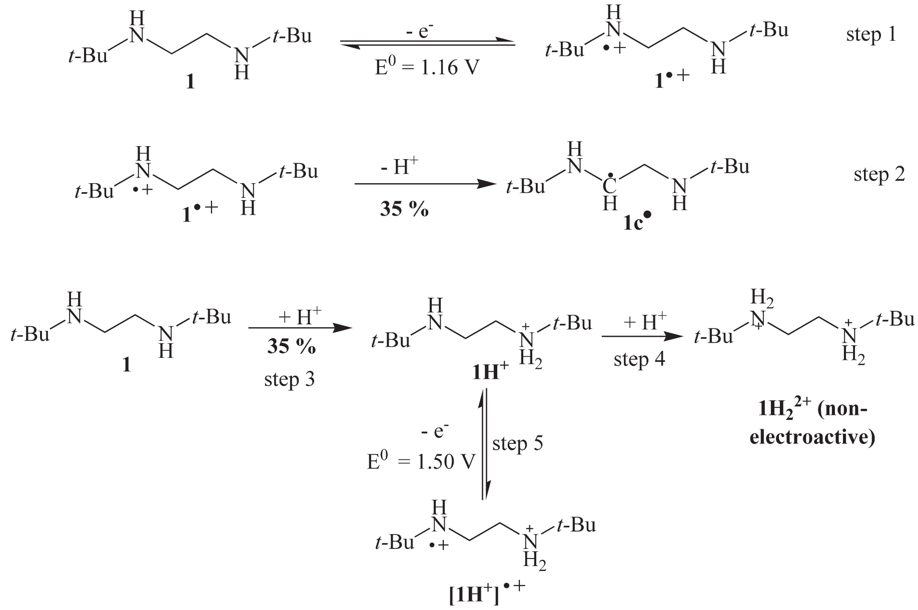
[16] Andrieux, C.-P.; Savéant, J. M. In *Electrochemical Reactions in Investigations of Rates and Mechanism of Reaction Techniques of Chemistry*; Bernasconi, C. F., Ed.; Wiley: New York, 1986; Vol. VI/4E, p 305.

SCHEME 3



around 1.45 V. The changes observed in the cyclic voltammograms of **1** in the presence of *n*-hexylamine are in good agreement with the initial hypothesis and confirm the capability of *n*-hexylamine for acting as a base.

Two possibilities could fairly explain the significant increase in the anodic current of the first anodic wave of **1** on addition of known amounts of *n*-hexylamine. As a first approach, the simultaneous oxidation of both equivalent functional amino groups present in the starting material should be taken into account. This mechanistic hypothesis would imply that bielectronic waves should be obtained within the entire scan rates range studied. However, monoelectronic processes were observed when reversibility was achieved. This finding led us to discard the initial hypothetic pathway. As a consequence, an ECE mechanism at the level of the first anodic wave would be a plausible explanation in good agreement with the experimental data available.

Cyclic Voltammetry in Acidic Media. The voltammetric measurements discussed herein were performed upon careful addition of known amounts of perchloric acid to a solution containing **1** (4.00 mM) in DMF + $LiClO_4$ 0.1 M. Due to the well-known basic character of functional alkyl amino groups, significant changes should be expected in the shape of the cyclic voltammograms of **1** upon addition of controlled amounts of perchloric acid. Thus, the addition of perchloric acid to a solution containing **1** should lead to solutions containing mixtures of **1**, $\mathbf{1H^+}$, and $\mathbf{1H_2^{2+}}$. The composition of these solutions will depend on the amount of acid added. At this point, it should be reminded that quaternary ammonium salts are nonelectroactive species within the potential range studied and no electrochemical response in the anodic scan should be expected due to the presence of $\mathbf{1H_2^{2+}}$. Hence, the addition of 0.5 equiv of perchloric acid to a solution containing **1** led to an equimolar mixture of $\mathbf{1/1H^+}$ which produced an important decrease in the first anodic peak at 1.13 V ascribed to the oxidation of **1**, in addition to a significant increase in the height of the second oxidation wave at 1.53 V. Further addition up to 1 equiv of perchloric acid should lead to a solution containing merely $\mathbf{1H^+}$. Under such experimental conditions, the cyclic voltammogram exhibited a unique monoelectronic wave at 1.53 V, which is in good agreement with the data reported in previous studies for species as $\mathbf{1H^+}$.[14] Scanning to negative potentials an irreversible cathodic peak due to the reduction of $\mathbf{1H^+}$ is observed at −2.65 V.[15] A residual anodic current still remains at 1.13 V when adding 1 equiv of perchloric acid suggesting the existence of acid−base based equilibriums which would be responsible for the presence of low amounts of **1** in solution.

According to the voltammetric results and going back to the electrochemical behavior of **1** in neutral media (DMF + $LiClO_4$ 0.1 M), we concluded that $\mathbf{1H^+}$ is unequivocally the species responsible for the second voltammetric signal observed for **1** at 1.53 V. The reversibility of this peak was reached by increasing the scan rate to 1.0 V s^{-1} with E_2^0 = 1.50 V. On the other hand, no voltammetric signal was obtained on addition of 2.0 equiv of perchloric acid which would be in good agreement with the nonelectroactive character previously predicted for $\mathbf{1H_2^{2+}}$. The evolution observed in the shape of the cyclic voltammograms recorded for **1** in neutral, basic, and acidic media could be readily rationalized as outlined in Scheme 3.

In neutral media, according to the electrochemical data obtained, $\mathbf{1^{\bullet+}}$ is formed at 1.16 V (step 1). Thus, as is widely accepted in the case of the anodic oxidation of alkyl monoamines containing C−H bonds in the α position to the nitrogen,[14,17] we concluded that the deprotonation of the radical cation $\mathbf{1^{\bullet+}}$ is the chemical reaction following the electron transfer (step 2). Such a result would be strongly supported by the hypothesis previously made by Evans for the electrochemical oxidation mechanism of DABCO, a tertiary cyclic alkyl diamine.[17] In neutral media, analysis of the cyclic voltamograms recorded for **1**, allowed us to

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[17] Zheng, Z.; Evans, D. H.; Nelsen, S. F. *J. Org. Chem.* **2000**, *65*, 1793–1798.

estimate from the height of that voltammetric signal at 1.50 V (step 5) that 35% of the starting material remains in solution in its monoprotonated form, **1H**$^+$ (step 3), by effect of the chemical reaction linked to the first electron transfer (step 2). In the presence of *n*-hexylamine acting as a base, step 3 consisting of the formation of the monoprotonated specie, **1H**$^+$, does not longer occur in contrast with the process described in acidic media for which steps 3, 4, and 5 were the most important. In summary, the deprotonation of the radical cation $\mathbf{1}^{\bullet+}$ through the Cα-H bond cleavage was clearly evidenced by the cyclic voltammetry results not only in acidic media but also in the presence of a weak base such as *n*-hexylamine.

In order to elucidate the overall mechanism associated to the electrochemical oxidation of **1** that enabled us to afford the aforementioned imidazolium salts, controlled potential electrolyses of **1** were carried out.

Controlled Potential Electrolyses of 1 in Neutral Media. Exhaustive oxidation of a solution containing 18.50 mM of **1** in DMF+ $LiClO_4$ 0.1 M was carried out by applying 1.20 V. Upon consumption of 1.0 F the anodic current reached negligible values close to 1−2 mA. An anodic scan recorded under these conditions exhibited a unique irreversible anodic peak located at 1.53 V previously assigned to the oxidation of **1H**$^+$. The concentration of **1H**$^+$ at the end of the electrolysis was readily estimated from the height of that voltammetric signal assuming a monoelectronic process. In addition, two reduction peaks located at −2.49 and −2.65 V when scanning to negative potentials appeared. The second cathodic wave was assigned to the reduction of **1H**$^+$ according to the cyclic voltammetry experiments performed in acidic media.[15] However, the nature of the first reduction peak located at −2.49 V was still unclear at this point. In order to obtain further information on the chemical process occurring during the anodic oxidation of **1**, analyses of these electrolyzed samples were subsequently carried out by GC−MS. Such a procedure first required a neutralization of the protonated species present in solution and their extraction with toluene. In doing so, not only was the supporting electrolyte removed from the organic layer but also the charged species that could be formed during the electrochemical process were missed. As a result, only the starting material in its neutral form, **1**, was detected by mass spectrometry at *m*/*z* value of 172. However, careful quantification of **1** using GC−MS and also ESI+ measurements confirmed that only 45% with respect to its initial concentration was recovered at the end of the process. The starting material quantified in the aforementioned electrolyzed samples is slightly higher than expected according to the previously described cyclic voltammetry experiments. These differences could be attributed to the longer time employed to carry out the exhaustive oxidation. This finding, that only **1** (45%) is recovered, suggested the idea discussed earlier that charged species were probably formed during the electrochemical process and that they would probably remain in the aqueous layer. Analyses of the freshly electrolyzed solutions carried out by ESI+ allowed us to detect the charged species that had not been extracted to the organic layer during the working-up procedure. A new signal appeared at an *m*/*z* value of 183 that could be assigned to an unknown charged species, **10** in 40% of yield (Table 1). Controlled potential electrolysis performed in DMSO under similar experimental conditions allowed us detect a new peak at *m*/*z* = 74 assigned to the presence of $^t\mathrm{BuNH_3}^+$ by ESI+.

TABLE 1. Products and Yields Obtained by Performing Controlled Potential Electrolyses of 1 (*c* = 18.5 mM) in DMF + $LiClO_4$ 0.1 M at 1.20 V

charge	% **1** (*m*/*z* = 172)	% **10** (*m*/*z* = 183)
1.0 F (without *n*-hexylamine)	45	40
1.8 F (**1**/*n*-hexylamine 1:1)	<1	93
0.8 F (**1**/*n*-hexylamine 1:1)	35	30[a]

[a] **19** has been detected and identified but not quantified.

Controlled Potential Electrolyses of 1 in the Presence of *n*-Hexylamine. To minimize the undesired protonation of the starting material which led to a decrease in the yield of the process, several controlled potential electrolyses were carried out in the presence of known amounts of *n*-hexylamine. This experimental strategy was specifically developed to take the advantage of the similar basic character attributed to **1** and *n*-hexylamine which would make the protonation of *n*-hexylamine more favorable since it is oxidized at more positive potentials than **1**.

To this end, solutions of **1** in the presence of 1 equiv of *n*-hexylamine were prepared in DMF. Their exhaustive electrochemical oxidation (1.8 F) was carried out at 1.20 V. Less than 1% of **1** was recovered, and the product **10** (*m*/*z* = 183) was obtained in good yield (90%) (Table 1). Chemical analysis of **10** by ^{1}H NMR, ^{13}C NMR, and ESI+ unequivocally confirmed its identity as 1,3-di(*tert*-butyl)-4,5-dihydro-1*H*-imidazolium perchlorate.[18] **10** shows a reduction peak potential at −2.49 V. This peak had been already observed by cyclic voltammetry upon exhaustive electrochemical oxidation of **1** at 1.20 V in neutral media.

Consumption of 0.8 F under the experimental conditions specified (DMF + $LiClO_4$ 0.1 M in the presence of 1 equiv of *n*-hexylamine) affords 35% of **1** and 30% of **10** and led to the detection of a heterocyclic neutral compound, **19**, detected by GC−MS at *m*/*z* = 184. The isolation of that compound was achieved, and the spectroscopic characterization is in good agreement with that reported in the literature for the 1,3-di-*tert*-butylimidazolidine, **19** (Table 1).[19] The new intermediate identified, **19**, is a heterocyclic tertiary diamine which would be readily oxidized at the potential applied according to the previous work reported by our group.[14,20]

The electrochemical behavior of the species included in Figure 1 is analogous to that observed for the secondary alkyl diamine, **1**. In particular, the extension of the exhaustive electrochemical oxidation in basic media to aliphatic diamines **2**−**9** led to analogous results as summarized in Table 2.

Either imidazolium or tetrahydropyrimidinium cations are obtained in all the cases investigated. The size of the ring formed depends on the number of methylene units forming the alkyl chain connecting the amino groups in the starting diamine. The good yields obtained and high selectivity of the overall process, particularly when symmetric diamines were

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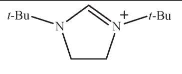
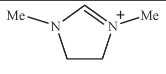
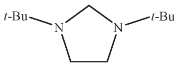
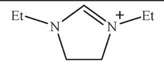
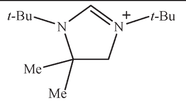
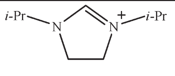
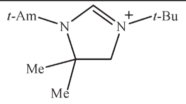
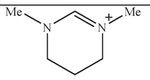
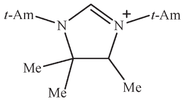
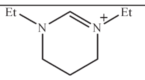
(18) Chemical synthesis of 1,3-di(*tert*-butyl)-4,5-dihydro-1*H*-imidazolium perchlorate (**10**) was performed as detailed in the Experimental Section.[16] Subsequent analysis by ESI+ and cyclic voltammetry unequivocally confirmed the identity of **10**.

(19) Denk, M. K.; Rodezno, J. M.; Gupta, S.; Lough, A. I. *J. Organomet. Chem.* **2001**, 242–253.

(20) Adenier, A.; Pinson, J.; Gallardo, I.; Vilà, N. *Langmuir* **2004**, *20*, 8243–8253.

TABLE 2. Summary of the Yields Obtained When Exhaustive Electrochemical Oxidation at 1.20 V of Solutions Containing Secondary Alkyl Diamines 1−9 in DMF + $LiClO_4$ 0.1 M in the Presence of *n*-Hexylamine (ConcentrationRratio 1:1)

DIAMINE	PRODUCT	YIELD (%)	DIAMINE	PRODUCT	YIELD (%)
1	 **10**	93	**5**	 **14**	92
	 **19**	(a)	**6**	 **15**	93
2	 **11**	45	**7**	 **16**	90
3	 **12**	41	**8**	 **17**	55
4	 **13**	35	**9**	 **18**	59

[a] **19** has been detected but not quantified by GC−MS as intermediate when electrolyses were performed consuming 0.8 F in the presence of *n*-hexylamine.

the starting material (**1**, **5**−**9**), makes the electrochemical process highly attractive in comparison to the conventional chemical methods previously described.[13b]

Mechanistic Proposal and Discussion. Since the electrochemical behavior for all the secondary alkyl diamines investigated displayed the same trend, we will particularly focus the detailed mechanistic discussion on **1**. Taking into account not only the nature but also the yields of the products and intermediate species obtained, two reaction pathways as outlined in Scheme 4 will be discussed.

The formation of the aforementioned *N*-heterocyclic cationic species in such a good yield cannot be rationalized by considering the deprotonation of the radical cation (Scheme 3 and route 1, Scheme 4) as the only first-order chemical reaction occurring at the radical cation level. Consequently, upon electrochemical oxidation of **1**, the corresponding radical cation $\mathbf{1}^{\bullet+}$ (step 0, Scheme 4) should evolve through two competitive first-order chemical reactions which would be simultaneously operative and would eventually result in the formation of identical final products. For this reason, the $C\alpha{-}C\beta$ bond cleavage (route 2, Scheme 4) should be taken into account for the radical cations described herein. In this sense, it should be mentioned that such a reaction has been previously proposed when radical cations of ethylenediamines have been photochemically generated.[21]

The deprotonation of $\mathbf{1}^{\bullet+}$ (step 1, Scheme 4) leads to a carbon-centered radical intermediate, $\mathbf{1_C}^{\bullet}$ which isomerizes to nitrogen-centered radical intermediate $\mathbf{1_N}^{\bullet}$.[14,20] In parallel, $\mathbf{1}^{\bullet+}$ undergoes a $C\alpha{-}C\beta$ bond cleavage (step 2, Scheme 4) affording a radical intermediate, $\mathbf{F_{C-C}}^{\bullet}$, and a cationic fragment $\mathbf{F_{C-C}}^{+}$. This cationic fragment has been detected by ESI+ at an *m*/*z* value of 86.

As outlined in step 1a, Scheme 4, we propose the formation of a neutral triamine (**TA**) by a coupling reaction between radical intermediate species $\mathbf{1_N}^{\bullet}$ and $\mathbf{F_{C-C}}^{\bullet}$ resulting from each type of cleavage postulated. The structure of **TA** contains a tertiary functional amino group that is readily oxidized at the potential applied (Step 1b, Scheme 4).[20] The corresponding radical cation ($\mathbf{TA}^{\bullet+}$) would evolve as expected through a $C_\alpha{-}H$ bond cleavage (step 1c, Scheme 4). The new carbon-centered radical ($\mathbf{TA}^{\bullet}$) would be oxidized

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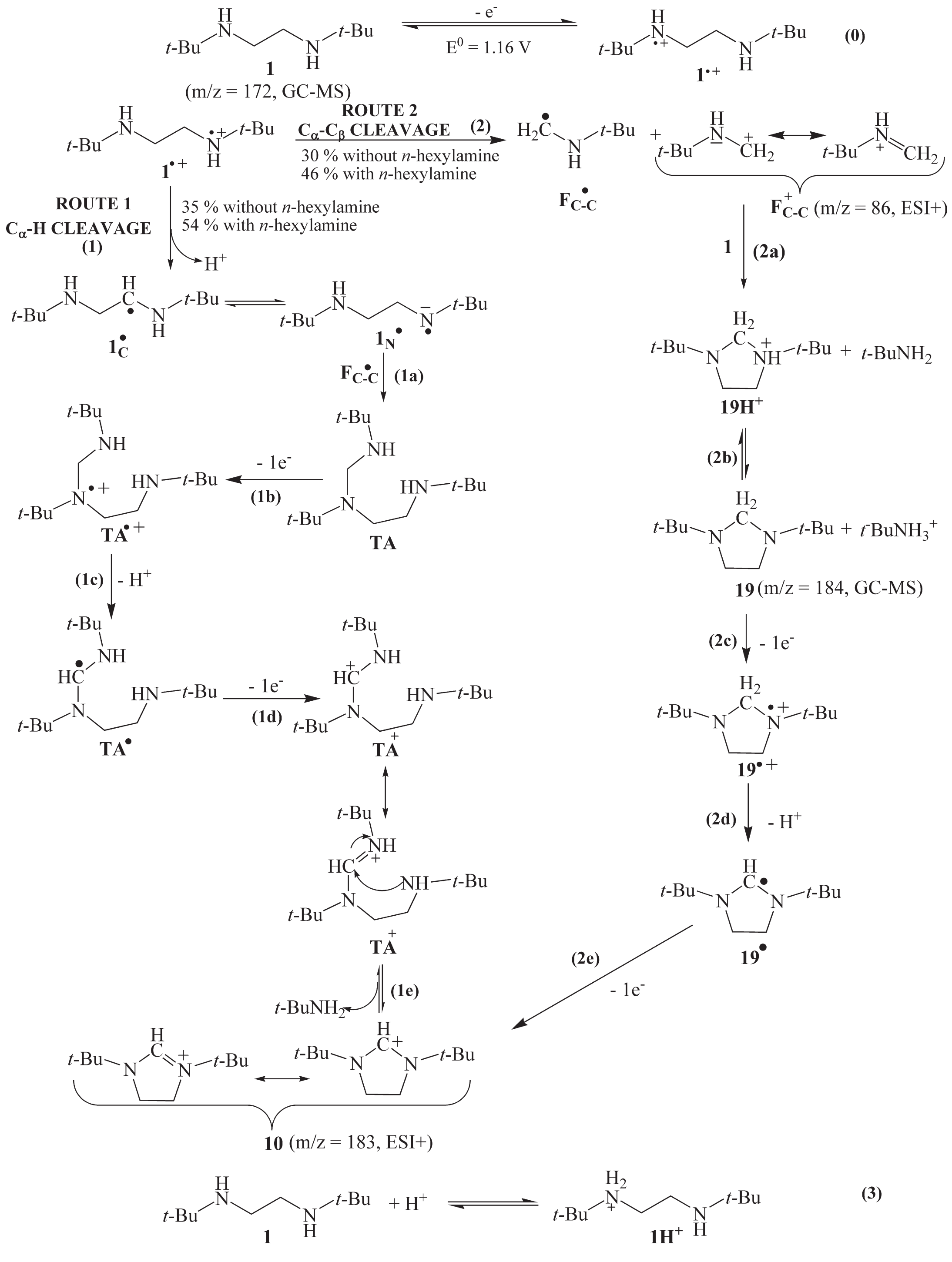
[21] (a) Gan, H.; Leinhos, U.; Gould, I. R.; Whitten, D. G. *J. Phys. Chem.* **1995**, *117*, 3566–3573. (b) León, J. W.; Whitten, D. G. *J. Am. Chem. Soc.* **1993**, *115*, 8038–8043. (c) Bergmark, W. R.; Whitten, D. G. *J. Am. Chem. Soc.* **1990**, *112*, 4042–4043. (d) Ci, X.; Whitten, D. G. *J. Am. Chem. Soc.* **1989**, *111*, 3459–3461. (e) Kellett, M. A.; Whitten, D. G *J. Am. Chem. Soc.* **1989**, *111*, 2314–2316. (f) Ci, X.; Lee, L. Y. C.; Whitten, D. G. *J. Am. Chem. Soc.* **1987**, *109*, 2536–2538. (g) Lee, L. Y. C.; Y. Ci, X.; Giannotti, C.; Whitten, D. G *J. Am. Chem. Soc.* **1986**, *108*, 175–177.

SCHEME 4



at the potential applied[22] (step 1d, Scheme 4) leading to a carbocation (**TA**$^+$) which would undergo a rearrangement and would afford **10** (m/z = 183) after elimination of a *tert*-butylamine molecule (m/z = 74) (step 1e, Scheme 4) detected by ESI+ when electrolysis were performed in DMSO instead of DMF.

On the other hand, a nucleophilic attack (Step 2a, Scheme 4) by the starting material, **1**, on the cationic fragment $\mathbf{F_{C-C}}^+$ coming from the $C_\alpha-C_\beta$ bond dissociation (route 2) would lead to a cyclic diamine in its monoprotonated form (**19H**$^+$) and a *tert*-butylamine molecule detected by ESI+ in DMSO. According to a slightly higher basic character reported for primary alkyl amino groups, an acid–base based equilibrium should be expected (step 2b,

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[22] Vilà, N. Ph.D. Thesis. Electrochemical studies of tertiary alkyl diamines responding to the molecular formula $(R_1R_2)NCH_2N(R_3R_4)$ evidenced that when the alkyl chain between the functional amino groups is limited to one methylene unit the carbon centered radical obtained is oxidized at the potential applied in contrast with the electrochemical behavior displayed for tertiary alkyl diamines with longer aliphatic chains connecting the functional amino groups.

Scheme 4). Such a cyclic diamine, **19** (m/z = 184), containing tertiary amino functional groups would be susceptible to being further oxidized (step 2c, Scheme 4) at the potential applied leading to its corresponding radical cation, $\mathbf{19}^{\bullet+}$, which would evolve through a deprotonation (step 2d, Scheme 4) and would undergo further oxidation to eventually afford the imidazolium cation **10** as well (step 2e, Scheme 4).

In neutral media, the protonation of the starting material leading to $\mathbf{1H}^+$ takes place (step 3, Scheme 4) and **10** is formed by electrochemical oxidation in 40% yields (Table 1). The addition of a base, such as *n*-hexylamine, to the media allowed us to notably enhance the yields of the imidazolium salt obtained. The presence of *n*-hexylamine, a primary amine with a similar pK_a value to the secondary alkyl diamines studied but significantly more difficult to oxidize, plays a key role since it eventually acts as a base reacting with the protons generated via deprotonation of the corresponding radical cation and inhibiting the formation of $\mathbf{1H}^+$ (step 3, Scheme 4).

Since electrochemical data indicates that in neutral media the deprotonation of $\mathbf{1}^{\bullet+}$ contributes 35% to its decomposition, it could be thought that the Cα-Cβ bond dissociation would contribute 30% in the absence of a base. Such contributions could be rationalized considering that $\mathbf{1}^{\bullet+}$ is formed only at 65% due to the protonation of the starting material in a 35%. As mentioned above Cα-H contribution can be readily estimated from the height of the second anodic wave observed in neutral media which corresponds to the 35% expected for a monoelectronic process. Thus, the concentration of the monoprotonated alkyl diamine, $\mathbf{1H}^+$, has been determined from the height of such an anodic wave assuming a monoelectronic process. Subsequently, this measurement indirectly serves to estimate the Cα−Cβ bond dissociation contributing to the decomposition of $\mathbf{1}^{\bullet+}$ from the mass balance for **1** as follows: $[\mathbf{1H}^+] = [\mathbf{1}_\mathbf{C}^\bullet] = 0.35$ and $[\mathbf{1H}^+] + [\mathbf{1}_\mathbf{C}^\bullet] + [\mathbf{1}^{\bullet+}] = 1.0$, thus $[\mathbf{1}^{\bullet+}] = 0.30$.

In basic media, the contribution of both first order chemical reactions in competition can be corrected. Accordingly, the new values would be 54% (C_α−H) and 46% (C_α−C_β) instead of the initial 35 and 30%, respectively (steps 1 and 2, Scheme 4). In conclusion, when adding a base to the media no significant changes in the contributing ratios between both competitive reactions were estimated and a contribution of ca. 50% was assumed for each chemical reaction.

Estimation of the number of electrons involved in the overall process is greatly facilitated by considering both mechanistic pathways (routes 1 and 2) separately and taking advantage of the contribution of each process to the final products estimated as described above.

As depicted in route 1 (Scheme 4), two electrons per molecule are involved in the process as follows:

$$2(\mathbf{1}) - 4e^- \rightarrow \mathbf{10} + \mathrm{F_{C-C}}^+ + {}^t\mathrm{BuNH_2} + 2\mathrm{H}^+$$

In contrast, in route 2, one and a half electrons would be involved in the process:

$$2(\mathbf{1}) - 3e^- \rightarrow \mathbf{10} + \mathrm{F_{C-C}}^\bullet + {}^t\mathrm{BuNH_3}^+ + \mathrm{H}^+$$

Table 3 summarizes the number of electrons involved in each process taking into account the contribution of each reaction pathway to afford **10**. Theoretical and experimental values are in good agreement. The theoretical data has been calculated from the sum of the number of electrons involved in each reaction pathway either in neutral or basic media according to Scheme 4.

TABLE 3. Electrons Involved in the Overall Process Taking into Account the Fact That Both Mechanistic Pathways Are Simultaneously Taking Place

	$1_N^\bullet + \mathrm{F_{C-C}}^\bullet$ route 1		$1 + \mathrm{F_{C-C}}^+$ route 2		electrons	
chemical reaction	%	no. of e^{-a}	%	no. of e^{-b}	theor[c]	exp[d]
Neutral media	35	2 × 0.35 = 0.7	30	1.5 × 0.30 = 0.45	1.15	1.3
Basic media	54	2 × 0.54 = 1.1	46	1.5 × 0.46 = 0.70	1.80	1.8

[a] Electrons transferred according to the mechanistic proposals outlined in Scheme 4 (route 1, $2e^-$) [b] Electrons transferred according to the mechanistic proposals outlined in Scheme 4 (route 2, $1.5e^-$). [c] no. of e^{-a} + no. of e^{-b}. [d] Electrons transferred according to cyclic voltammetry data.

Significant lower yields were obtained for diamines **2**−**4**, **8**, and **9** (Table 2). In these particular cases, one of the reaction pathways proposed, routes 1 and 2, did not occur. It should be noted that alkyl diamines **2**−**4**, are nonsymmetric species with a higher degree of steric hindrance that most likely makes it more difficult for the nucleophilic attack by the starting material on the cationic fragment obtained through route 2. Furthermore, if such a reaction was taking place an additional final product C2-position substituted would be obtained. Byproducts coming from this process have never been detected. On the other hand, for diamines **8** and **9**, the coupling reaction between radicals proposed in route 1 (step 1a) would lead to a stable triamine with functional amino groups connected by longer alkyl chains displaying a different reactivity as previously reported.

Concluding Remarks

A novel one-pot electrosynthetic route has been developed to afford imidazolium and tetrahydropyrimidinium cationic derivatives from secondary alkyl diamines in yields of 35−93%. Either imidazolium or tetrahydropyrimidinium cations are obtained in all the cases investigated. The most optimum experimental conditions have been established when symmetrical secondary alkyl diamines have been employed as starting material in basic media leading to the best yields of the cationic species obtained. In those cases, not only the good yields but also the high selectivity of the overall process makes the electrochemical methodology much more attractive than the conventional and much longer procedures previously described.[13b] The size of the ring formed depends on the number of methylene units forming the alkyl chain connecting the amino groups in the starting diamine.

Furthermore, the results reported here represent a novel advance in the understanding of the overall mechanistic processes taking place on electrochemical generation of radical cation from secondary ethylene- and propylenediamines from the cyclic voltammetry and controlled potential electrolysis experiments performed. In this sense, it should be highlighted that our synthetic results (nature of the final products obtained, intermediate species detected and also yields of at least 50% of the cationic species) have been rationalized by establishing a competitive reaction pathway based on the coexistence of two first-order chemical reactions simultaneously occurring at the radical cation level.

In summary, a new versatile electrochemical procedure to afford imidazolium and tetrahydropyrimidinium cations based ionic liquids has been developed via anodic oxidation of secondary alkyl diamines.

Experimental Section

General Considerations. DMF, *n*-Bu_4NBF_4, and *n*-Bu_4NPF_6 were from commercial sources and used without further purification.

Starting Materials. *N*,*N*′-Di-*tert*-butylethylenediamine (**1**), *N*,*N*′-dimethylethylenediamine (**5**), *N*,*N*′-diethylethylenediamine (**6**), *N*,*N*′-diisopropylethylenediamine (**7**), *N*,*N*’-dimethylpropylenediamine (**8**), and *N*,*N*′-diethylpropylenediamine (**9**) were from commercial sources. *N*-*tert*-Butyl-2-*tert*-butylamino-2-methylpropionamide was prepared as previously reported by Lai.[23] *N*,*N*′-Di-*tert*-butyl-2-methyl-1,2-propylendiamine (**2**) was obtained by chemical reduction of the *N*,*N*′-Di-*tert*-butylamino-2-methylpropionamide by following the procedure recently reported.[14] *N*-*tert*-Butyl-*N*-*tert*-amyl-2-methyl-1,2-propylendiamine (**3**) and *N*,*N*′-di-*tert*-amyl-1,2-dimethyl-1,2-propylendiamine (**4**) were synthesized as previously described.[13b] Chemical synthesis of 1,3-di-*tert*-butyl-4,5-dihydro-3*H*-imidazol-1-ium tetrafluoroborate (**10**) was performed from *N*,*N*′-di-*tert*-buthylethylenediamine, ethereal tetrafluoroboric acid, and triethyl orthoformate using the procedure previously described in the literature.[13b] All the commercially available reactants were of the highest purity and used without further purification.

Instrumentation and Procedure. Cyclic Voltammetry. Commercial glassy carbon was used as a working electrode (diameter = 0.5 mm). A platinum disk electrode was used as a counter electrode (diameter = 1 mm). Electrochemical measurements were performed as previously described.[14] All potential measurements were measured and quoted vs SCE separated from the solution by a double frit system containing either *n*-$Bu_4NBF4.0.1$ M. Prior to the electrochemical measurements, the glassy carbon surface was cleaned by polishing with 1 μm diamond paste. After polishing the electrode was rinsed with ethanol.

General Procedure for the Electrosynthesis of Substituted Imidazolinium and Tetrahydropyridinium Perchlorate and Hexafluorophosphate Salts 10−18. Electrochemically initiated syntheses were performed using a potentiostat in a dark (“brown glassware”) conical three-electrode cell equipped with a methanol jacket. The temperature was fixed to 10 °C in all cases by means of a thermostat. A graphite rod was used as the working electrode, while a platinum bar and SCE were separated from the solution by a double frit system containing $LiClO_4$ 0.1 M. Under an argon atmosphere, a controlled potential electrolysis was carried out in a solution of **1** (0.20 mmol) in DMF containing $LiClO_4$ 0.1 M as a supporting electrolyte at 1.20 V. The anodic current reached a plateau value close to zero when 95% of the theoretical charge, assuming a monoelectronic process, was consumed. At the end of the anodic oxidation process, the electrolyzed samples were poured into 10 mL of a sodium hydroxide aqueous solution (0.05 M). The resulting aqueous mixture was extracted three times with 10 mL of toluene. The organic layers were dried with sodium sulfate and then concentrated in vacuo. The residue was distilled at low pressure and **1** was recovered as a colorless liquid (45%). However, analysis of the freshly electrolyzed solutions by positive-ion mode electrospray ionization (ESI+) and elemental analysis led us to identify and quantify **10**. When the electrochemical synthesis was carried out in acetonitrile, **10** was isolated by precipitation of the hexafluorophosphate derivative taking advantage of its low solubility in that solvent.

1,3-Di-*tert*-butyl-4,5-dihydro-3*H*-imidazol-1-ium Hexafluorophosphate, 10. ^1H NMR ($CDCl_3$, 250 MHz, δ ppm): 1.39 (s, 9 H), 2.05 (s, 9 H), 3.27 (m, 2 H), 3.78 (t, 2 H) 7.72 (s, 1 H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 27.6, 35.0, 40.7, 45.9, 47.0, 141.2. ESI+ *m*/*z*: 183.1 (18), 127.1 (100), 71.3 (48). Anal. Calcd for $C_{11}H_{23}F_6N_2P$: C, 40.25; H, 7.06; N, 8.53. Found: C, 40.35; H, 7.11; N, 8.62.

1,3-Di-*tert*-butyl-5,5-dimethyl-4,5-dihydro-1*H*-imidazol-3-ium Hexafluorophosphate, 11. Compound **11** was electrochemically synthesized from *N*,*N*′-di-*tert*-butyl-2-methylpropylenediamine, **2**, by an electrochemical procedure analogous to those described in the previous section. ^1H NMR ($CDCl_3$, 250 MHz, δ ppm): 1.50 (s, 9 H), 2.10 (s, 9 H), 2.35 (s, 6 H), 3.95 (m, 2 H), 7.85 (s, 1 H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 27.6, 35.0, 40.7, 45.9, 47.0, 141.2. ESI+ *m*/*z*: 253.1 (12), 183.1 (100), 113.1 (52), 99.2 (48), 71.3 (35). Anal. Calcd for $C_{13}H_{27}F_6N_2P$: C, 43.82; H, 7.58; N, 7.87. Found: C, 43.55; H, 7.81; N, 8.02.

1-*tert*-Amyl-3-*tert*-butyl-5,5-dimethyl-4,5-dihydro-3*H*-imidazol-1-ium Hexafluorophosphate, 12. Compound **12** was electrochemically synthesized from *N*-*tert*-butyl-*N*′-tert-amyl-2-methylpropyelenediamine, **3**, by an electrochemical procedure analogous to those described in the previous section. ^1H NMR ($CDCl_3$, 250 MHz, δ ppm): 0.85 (t, 3 H), 1.15 (s, 6 H), 1.30 (qd, 2 H), 2.05 (s, 15 H), 3.98 (m, 2 H), 7.72 (s, 1 H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 27.6, 35.0, 40.7, 45.9, 47.0, 141.2. ESI+ *m*/*z*: 225.1 (18), 169.1 (100), 99.3 (37), 71.3 (45) Anal. Calcd for $C_{14}H_{29}F_6N_2P$: C, 45.41; H, 8.15; N, 7.57. Found: C, 45.63; H, 8.23; N, 7.41.

1,3-Di-*tert*-amyl-4,5,5-trimethyl-4,5-dihydro-1*H*-imidazol-3-ium Hexafluorophosphate, 13. Compound **13** was electrochemically synthesized from *N*,*N*′-di-*tert*-amyl-2-methyl-2,3-butylenediamine, **4**, by an electrochemical procedure analogous to those described in the previous section. ^1H NMR ($CDCl_3$, 250 MHz, δ ppm): 0.84 (t, 3 H), 1.15 (s, 6 H), 1.42 (s, 6 H), 1.51 (qd, 2 H), 1.60 (t, 3 H), 1.76 (d, 3 H), 2.35 (s, 6 H), 3.85 (qd, 2 H), 4.56 (qd, 1 H), 8.10 (s, 1 H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 27.6, 35.0, 40.7, 45.9, 47.0, 141.2. ESI+ *m*/*z*: 253.1 (12), 183.1 (100), 113.1 (52), 99.2 (48), 71.3 (35). Anal. Calcd for $C_{16}H_{33}F_6N_2P$: C, 48.24; H, 8.29; N, 7.04. Found: C, 48.50; H, 8.47; N, 6.97.

1,3-Dimethylimidazolinium Hexafluorophosphate, 14. Compound **14** was electrochemically synthesized from *N*,*N*′-dimethylethylenediamine, **5**, by an electrochemical procedure analogous to those described in the previous section. ^1H NMR ($CDCl_3$, 250 MHz, δ ppm): 2.65 (s, 3 H), 3.25 (s, 3 H), 3.55 (m, 4 H), 7.07 (s, 1 H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 35.2, 38.7, 51.0, 51.3 140.0.

1,3-Diethylimidazolinium Hexafluorophosphate, 15. Compound **15** was electrochemically synthesized from *N*,*N*′-diethylethylenediamine, **6**, by an electrochemical procedure analogous to those described in the previous section. ^1H NMR ($CDCl_3$, 250 MHz, δ ppm): 0.99 (t, 3 H), 1.27 (t, 3 H), 2.44 (qd, 2 H), 3.69 (qd, 2 H), 3.60 (m, 4 H), 7.33 (s, 1 H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 9.8, 11.4, 43.2, 47.1, 49.2, 49.5, 151.4.

1,3-Diisopropylimidazolinium Hexafluorophosphate, 16. Compound **16** was electrochemically synthesized from *N*,*N*′-diisopropylethylenediamine, **7**, by an electrochemical procedure analogous to those described in the previous section. ^1H NMR ($CDCl_3$, 250 MHz, δ ppm): 1.06 (d, 6 H), 1.48 (d, 6 H), 2.04 (m, 1 H), 3.59 (m, 4 H), 4.20 (hp, 1 H), 7.60 (s, 1 H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 19.3, 22.1, 48.1, 51.9, 54.9, 118.7.

1,3-Dimethyl-1,4,5,6-tetrahydropyrimidin-3-ium Hexafluorophosphate, 17. Compound **17** was electrochemically synthesized from *N*,*N*′-dimethylpropylenediamine, **8**, by an electrochemical procedure analogous to those described in the previous section. ^1H NMR ($CDCl_3$, 250 MHz, δ ppm): 1.87 (s, 3 H), 2.36 (m, 2 H), 2.83 (m, 2 H), 3.25 (s, 3 H), 8.25 (s, 1 H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 37.5, 56.5, 52.2, 27.7, 158.3. ESI+ *m*/*z* (%): 113.1 (100).

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(23) Lai, J. T. *J. Org. Chem.* **1980**, *45*, 3671–3673.

1,3-Dimethyl-1,4,5,6-tetrahydropyrimidin-3-ium Hexafluorophosphate, 18. Compound **18** was electrochemically synthesized from *N*,*N*′-diethylpropylenediamine, **9**, by an electrochemical procedure analogous to those described in the previous section. ^{1}H NMR (CDCl$_3$, 250 MHz, δ ppm): 0.96 (t, 3 H), 1.23 (t, 3 H), 1.77 (m, 2 H), 2.46 (qd, 2 H), 3.25 (m, 2 H), 3.89 (qd, 2 H), 4.37 (m, 2 H), 8.26 (s, 1 H). ^{13}C NMR (CDCl$_3$, 100 MHz, δ ppm): 37.5, 56.5, 52.2, 27.7, 158.3. ESI+ m/z: 141.1 (100), 112.2 (18).

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Supporting Information Available: Characterization of the compounds including NMR spectra and MS data of the products. This material is available free of charge via the Internet at http://pubs.acs.org.